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3,786,133

TITANIUM CARBIDE PREPARATION

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No Drawing. Filed Sept. 11, 1970, Ser. No. 71,352

Int. Cl. C01b 31/30

U.S. Cl. 423-440

5 Claims

ABSTRACT OF THE DISCLOSURE

Preparation of TiC from impure titanium oxide containing starting materials by using a carburizing process involving a catalyzer, a binder, a controlled heating speed and temperature, whereby pure titanium carbide grains having high combined carbon and low free carbon contents are obtained as one phase and a metallic matrix surrounding the titanium carbide as another phase. The metallic matrix is readily removed from the two phase body by leaching, thereby recovering the pure titanium carbide.

This invention relates to a production of titanium carbide; more particularly, this invention relates to a process for preparing titanium carbide from impure titanium oxide containing starting material such as Sorelslag, ilmenite, perovskite, impure rutile, etc., whereby titanium carbide of high purity and exceptionally low carbon content is obtained from the starting material; this invention also relates to an intermediate product comprised of titanium carbide dispersed or surrounded in a matrix of a metal mixture formed from some of the metal oxides in the starting material mixture, this material, as such, has a number of uses.

In the production of titanium carbide from titanium oxide, it has been the desideratum to obtain a highly pure titanium carbide having a low free carbon content when starting from a low grade titanium oxide material such as Sorelslag, ilmenite, perovskite, etc. These titanium oxide containing materials contain a relatively high amount of impurities such as oxides of magnesium, calcium, aluminum, silicon and iron. In the titanium carbide production, removal of these impurities has been attempted by a number of processes.

In general, titanium carbide is produced by using a titanium oxide (TiO₂) containing material previously mentioned as a raw material, grinding it to a certain particle size, admixing the same with a carbonaceous material such as coke, carbon, finely divided and calcined petroleum coke, sawdust, etc., shaping this mixture with the aid of a binder such as pitch, molasses, etc. and reacting (carburizing) it at a temperature generally in the range from 1400° C. to 3000° C. most prevalently in the range from 1400° C. to 2000° C. Although the binder materials contain a number of constituents, the effect of these constituents on the carburization reactions has been subject only to speculation.

In most processes, the heating is effected in a resistance type of furnace or furnaces of similar kind; and the product obtained from these impure starting materials generally is a form of crude titanium carbide admixed with free carbon and a mixture of carbides formed from the impurities. In turn, this crude titanium carbide starting material has been used as a source of raw material for the production of titanium metal or titanium dioxide.

If a pure titanium carbide material is sought which can be used as a hard material for making tools, abrasives, or high temperature resistance elements, then titanium carbide is mostly produced by using pure titanium dioxide as a starting material or using a purified grade of titanium oxide ore such as purified rutile which consists of about 98% of titanium dioxide.

A further requirement for producing pure titanium carbide is a carbon of high purity, finely ground and calcined. Thus, low ash reducing agents such as petroleum coke are usually employed. Hence, the requirement for using highly pure starting materials in titanium carbide production has prompted a number of attempts to obtain pure titanium carbide from a low grade titanium bearing material. However, heretofore a method has not been discovered which would produce pure titanium carbide from impure starting materials as well as a purification process especially adaptable for obtaining TiC with a high combined and a low free carbon and for ready separation and removal of the impurities from titanium carbide.

Thus, a problem in the direct preparation of pure titanium carbide from impure starting materials has been that many oxides besides titanium oxides are contained in these starting materials. These impurities are oxides such as magnesium, calcium, aluminum, silicon and iron. If these materials are reduced and carburized in a graphite resistance furnace by the conventional processes, these oxides are carburized or carburized along with the titanium carbide. The final result is a multi-carbide product of low quality because of the undesirable properties imparted by these carbide impurities such as reduced hardness, melting point and stability, etc. Additionally, often large amounts of free carbon are present in the titanium carbide.

For use in the making of cutting tools and for use as a pure material, titanium carbide containing excessive amounts of the above-mentioned contaminants is unsuitable. Hence, the impure titanium carbide products have been used in the preparation of titanium metal or titanium pigment, thus requiring added processes to upgrade these starting materials. From the above, it follows that in order to utilize more economically an impure titanium oxide containing starting material, no intermediate processes can be tolerated which result in a titanium carbide of low quality, cause the formation of free carbon in titanium carbide, or result in impurities incapable of removal from the starting material.

It has now been found that a highly pure titanium carbide can be produced which has a high combined carbon content, a very low free carbon content, and which uses as a starting material an impure titanium oxide containing material.

Moreover, it has been found that the production of the highly pure titanium carbide can be achieved in a conventional graphite resistant furnace without the need for modifying the same; furthermore, it has been found that the product obtained in this particular carburization-reduction process contains the impurities in a form especially suitable for dissolving or leaching by means of a weak sulfuric acid and/or a weak hydrofluoric acid solution, the combination of both acids is especially advantageous.

Thus, it has been found that the carburizing process if carried out according to the novel method in which the impurities aid in the purification of titanium carbide and when employing a catalyst and a binder, produces an intermediate material capable of further purification and especially adaptable for producing titanium carbide usable in applications requiring pure or high grade titanium carbide.

Accordingly, it has been found that this up-grading of impure titanium containing starting material can be achieved successfully when a formulated starting composition is rapidly heated to a reaction condition which causes volatilization of some of the impurities, a formation of somewhat rounded titanium carbide particles and the reduction of the non-volatile impurities, and surrounding of the titanium carbide grains by a secondary metal or

matrix phase. This secondary phase or matrix is composed of a metal mixture or alloy of impurities in a form especially adaptable for removal by leaching after grinding the intermediate product. The reduced impurities are in a form which leaves these substantially in their metallic state. Additionally, this crude carbide containing the titanium carbide and secondary phase or matrix material has also high electric conductivity, and a high melting point. It can be used as a grinding material in grinding wheels, as electrodes, or as heat-resistant material, as well as for surface hardening.

As the result of X-ray studies and microprobe analysis, the titanium carbide product obtained for example from Sorelslag shows no detectable impurities within the titanium carbide grain; the secondary matrix consists of reduced impurities such as metallic Fe, Al, Si and some Ti. Impurities such as Mg, S, Mn, K, P, and Ca have been removed by volatilization and/or distillation. It is also observed that the content of Al, Si, and Fe in the phase, reduced material has been slightly decreased after the carburization step. In the reduced product, sodium chloride is present in very small amounts, e.g. 0.010% after reacting at 2500° C. Instead of Sorelslag, starting materials similar to it can be used in this process such as the previously recited low grade titanium oxide containing materials.

Although the exact mechanism by which the improved result has been achieved is not known, it is postulated, for the sake of clarity but not as an inviolable rule, that the impurities are caused first to volatilize and/or distill and then caused to form a metal matrix as the result of an addition of an alkali chloride preferably sodium chloride which apparently catalyzes the carburization reaction as well as the impurity conversion-reducing reaction. It is possible that this stepwise catalyzed removal of impurities prevents the formation of carbides and aids in converting into a volatile product, those impurities which are readily reduced at lower temperature and also aids in reducing those impurities which help in the refining of titanium carbide. Also, it is possible that rapid heating causes the formation of a relatively high amount of CO gas at high temperature, a condition which favors the formation of high combined carbon in titanium carbide. Thus, in order to obtain a pure TiC when using a low grade TiO₂ as the starting material, it has been found that a sodium chloride catalyzer in combination with rapid heating rate and proper temperature produces the pure TiC grain.

Still further, if carburization is carried out in the presence of sodium chloride, prolonged carburization does not cause an increase in free carbon; however, prolonged carburization in the absence of sodium chloride increases the free carbon content. The reduced and nonvolatile impurities are converted into a secondary metal matrix phase which has an apparent capability for refining the titanium carbide and for providing a better medium for carbon diffusion and for its uniform distribution.

To sum up, it is postulated that sodium chloride aids in removing impurities from titanium carbide and also in the formation of the titanium carbide. Thus, in the TiC production, according to the method herein, a metal matrix is formed after a step-wise volatilization of some of the impurities. This mixed, multi-phase metal matrix contains substantial amounts of iron, silicon and aluminum which appears to aid the purification of titanium carbide. As a result of first co-fluxing of the distillable on volatile impurities, secondly creating a strong carburizing atmosphere during titanium carbiding, and thirdly the formation of a metal alloy matrix which seems to soak up the impurities to provide better carbon diffusion and further enhances the separation of the titanium carbide phase from the secondary, metal phase, a highly pure titanium carbide is produced from an impure low grade titaniferous material. Also, the interface between carbon and titanium dioxide is better because of the shrinkage

of an extruded shape in the presence of sodium chloride. As a result of these competing phenomena, the unleached product is about 50% of the weight of the starting material. The matrix or secondary phase can be readily identified as the secondary phase is a metallic material which shows a whitish metal appearance whereas the titanium carbide grains are grey. As a consequence of the discovery, and as an example, titanium carbide of 99% purity, having 19.6% of combined carbon and less than 0.15% free carbon, is obtained from a low grade titanium dioxide material in a single step. The theoretical value of maximum combined carbon is 20.5%.

The process by which the improved results are obtained is carried out as follows. Titanium oxide in the form of an impure grade material such as Sorelslag, rutile, ilmenite, perovskite, is finely ground such that a starting material may have a mesh size from —100 mesh to —400 mesh. Graphite of about —100 mesh to about —400 mesh is admixed therewith and then admixed with flour or other suitable binders such as tar, molasses, etc. Included in this mixture is an alkali chloride catalyst in an aqueous solution. As sodium chloride is the least expensive material, it constitutes the desired catalyst.

A suitable range of the titanium containing material and carbon in the starting mixture should be in the proper ratio to reduce the oxides and form TiC; the flour binder from 3% to 10% weight in the mixture and the alkali chloride from 0.5% to 2% weight in the mixture.

An example of a suitable composition is of the following proportions: 683 parts of ground Sorelslag, about 251 parts of carbon as graphite, about 56 parts of flour and 10 parts alkali chloride (as NaCl) and 204 parts of water. Generally, Sorelslag consists of the constituents in the following exemplary ranges.

TABLE I.—SORELSLAG COMPOSITION

	Percent
TiO ₂ (total Ti as TiO ₂)	70–72
Ti ₂ O ₃ as TiO ₂	10.0–15.0
FeO	12.0–15.0
Met. Fe	¹ 1.5
SiO ₂	3.5–5.0
Al ₂ O ₃	4.0–6.0
CaO	¹ 1.2
MgO	4.5–5.5
Cr ₂ O ₃	¹ 0.25
V ₂ O ₅	0.5–0.6
MnO	0.2–0.3
C	0.03–0.10
S	0.03–0.10
P ₂ O ₅	¹ 0.05

¹ Maximum.

The above mixture of Sorelslag, carbon, flour and sodium chloride is extruded as a rod or in any other suitable form. A rod of about 10 cm. diameter formed at 20 to 40 kg./cm.² of pressure has been conveniently employed. An extruded briquette was held at 120° C. for 3 hours, then reacted at 2200° C. to 2600° C. for about 10–15 minutes with 20 to 50 minutes to heat up in a graphite induction furnace. Moreover, upon normal cooling the free carbon content does not appear to increase.

A continuous or a batch process may be employed. In a continuous process according to means well known in the art, care must be taken that the rod or shape which is being reduced and carbided is self-supporting and not friable. The amount of carbonaceous material added depends upon the required stoichiometric proportion for forming the titanium carbide and for reducing the metallic impurities. No excess of carbonaceous material is provided. As a suitable solid carbonaceous material, graphite, coke, or petroleum coke is employed.

The carburization reaction is carried out in a neutral gas such as argon or helium, or in a reducing gas such as carbon monoxide, hydrogen, or, in vacuum.

As it has been mentioned before, the rapid heating and the treatment at the desired temperature for about 15 minutes for a 10 cm. diameter briquette is found to be especially suitable for producing the carburized product. Alternatively, the carburization or carbiding reaction may be monitored by the conversion rate of titanium oxide to carbide and the formation of the metallic matrix. It is preferred that the starting material is heated at a rapid rate such that the desired temperature is achieved not later than after 70 minutes after the starting material has been introduced into a furnace. Generally, a heating rate of from 100° C./min. to 36° C./min. from the calcining temperature upwardly is suitable, a preferred rate is 70° C./min. to 50° C./min. It is postulated that the short reduction time increases the combined carbon in titanium carbide and decreases the free carbon. Slow heating appears to decrease the combined carbon content in the product.

It has been found advantageous to carry out the titanium reduction and carburization under a neutral atmosphere such as that provided by argon. A reducing atmosphere or vacuum may also be employed.

It has been found that with an increase in temperature, the amount of titanium in the reduced product first increases and then decreases, with about 2500° C. $\pm$ 100° C. offering the best operating range. With increased temperature, the amount of free carbon is decreased proportionately. Also, with increased temperature, the amount of impurities such as magnesium, calcium, sulfur and phosphorus have disappeared, while some of the iron, silicon and aluminum is vaporized. Thus, a better refining effect has been obtained at higher temperature which also aids in volatilization of the impurities.

For example at a temperature of 2500° C. and after treating for ten minutes a mixture of Sorelslag and the carbonaceous material, the reaction product contains relatively large titanium carbide grains of approximately 0.05 millimeters in diameter having little porosity. However, if the temperature is increased to 2800° C. for the same treatment time, the titanium carbide grains become larger and more porous. Further, if the temperature exceeds 2700° C., the extruded starting material melts and picks up carbon (0.5 to 9%) from the graphite crucible to form a eutectic. To remove the formed free carbon, it would be necessary to apply another, complicated purification process.

Thus, the size of the grains can range from 0.01 to 0.2 millimeters in diameter and can be adjusted by adjusting the temperature. It has also been found that if the treating time is varied, the grain size can be made to vary accordingly.

As a suitable furnace, a resistance type, induction, arc, etc., furnace may be employed. The product obtained in the carburization step is crushed in a conventional manner to expose the matrix to the leaching medium. Generally, a crushed material of a mesh size less than about 100 mesh is suitable. However, the desired mesh size is usually based on the size required for the final pure product. The carburized product and the metal matrix are leached at about 70° C. with an aqueous solution such as 1% to 3% sulfuric acid H₂SO₄, preferably 2% H₂SO₄ or 0.5 to 1% hydrofluoric acid HF, preferably a mixture of the two acids. The best results have been obtained when mixing the two leaching solutions and using them on the carbided product. These acids, in mixture, leach out the metallic matrix without attacking the titanium carbide.

After the leaching has been effected as determined by residual amounts of metal, the pure titanium carbide grains are collected as a residue. The grains are of a fine spherical type of various sizes which may be ground according to need. It is also observed that conventionally produced titanium carbide is usually crushed and ground which results in irregularly shaped grains.

According to this invention, highly pure titanium carbide is obtained which, after the leaching step, by means

of the leaching agents illustrated above, contains from 0 to 0.2% free carbon and about 19.7% combined carbon and 79.5% titanium. Moreover, titanium carbide produced according to this invention has a hardness from about 3500 (50 g. load) to 4200 V.H.N. (no crack load) which is the standard hardness range for a pure titanium carbide. In distinction from the final product, the matrix (Fe-Si-Al) surrounding the TiC has a hardness from approximately 900 (50 g. load) to 1300 V.H.N. After reacting, e.g. at 2500° C., the final matrix is composed of about 75% Fe, about 14% Si, and about 11% of Al. The matrix does not contain any detectable or significant amounts of carbides of these metals. The matrix also helps in grinding the titanium carbide.

The following has been included herein to illustrate the invention. Sorelslag of the following composition has been used as finely ground starting material.

TABLE II

Composition:	Percent by weight
TiO ₂ (total Ti as as TiO ₂)	71.3
Ti ₂ O ₃ as TiO ₂	11.00
FeO	10.70
Met. Fe	0.80
CaO	0.82
MgO	5.27
Al ₂ O ₃	4.67
SiO ₂	5.15
V ₂ O ₅	0.57
ZrO ₂	0.02
Cr ₂ O ₃	0.16
MnO	0.23
S	0.06
C	0.20
P ₂ O ₅	0.04

A mixture of 683 parts of the above defined material sized at approximately -320 mesh, 251 parts of finely ground graphite at -320 mesh, 56 parts of flour at -320 mesh and 10 parts of NaCl was prepared by admixing these components with 204 parts of water. This mixture was then extruded in a rod form as an 8 cm. diameter briquette at a pressure from 20 to 40 kg./cm.². The mixture may also be extruded or compacted in different size or forms as long as the shape permits the volatilization of impurities at the desired temperature. The extruded rod was then treated at 2500° C. for about 10 minutes in a graphite tube induction furnace. After this carburization step, a bright, metallic rod was recovered from the furnace which weighed about 50% less after carburization. After crushing to about a -2.5 μ (F.S.S. No.) size, the product was leached in an acid solution of 2% sulfuric (ranging from 1 to 2%) and 0.5% hydrofluoric acid (ranging from 1 to 0.3%). With a 1% H₂SO₄ and 1% HF solution at 70° C. for 3 hours, the residue contained 79.3% Ti, 19.75% combined carbon, 0.05% free carbon, 0.1% oxygen, 0.04% Zr, 0.5% V, 0.18% Fe, with Si, Mg, Ca, Al not detectable. With 2% H₂SO₄ at room temperature for 24 hours, the residue contained 0.50% Fe, less than 0.079% Si, less than 0.07% Al, non-detectable Mg, Ca, S.

With a 1% HF solution at room temperature for 24 hours, the residue contained 0.15% Fe, less than 0.03% Al, non-detectable Si, Mg or Ca.

From the above analysis it is evident that a starting material such as Sorelslag which contains the impurities such as magnesium oxide, calcium oxide, aluminum oxide, silica and iron oxides, when treated according to the present invention, results in a titanium carbide containing only traces of magnesium, calcium, and silicon, and minor amounts of aluminum, vanadium and iron. After leaching with sulfuric acid and hydrofluoric acid the residue contains no detectable amounts of aluminum or silicon. Purity of the titanium carbide products is also exceptionally good, i.e. from about 99 to 100%.

What is claimed is:

1. A process for producing highly purified titanium carbide from impure starting materials containing a titanium oxide consisting essentially of:

admixing with a titanium oxide containing material comprised of a titanium oxide, metallic iron, an iron oxide, aluminum oxide, magnesium oxide, calcium oxide, and silicon oxide, an alkali chloride in an amount from 0.5 to 2% by weight and a stoichiometric amount of carbonaceous material in reference to reducible metallic impurities and titanium carbide formed of graphite, coke, and petroleum coke and binder for the same in an amount from about 3% to 10% by weight to form a cohesive reaction admixture;

heating rapidly at a rate of 100° C./min. to 36° C./min. said admixture at a temperature within the range from 2000° C. to the melting point and for a period up to 20 minutes at the final temperature;

volatilizing from said admixture volatile impurities during the heating period;

reducing non-volatile impurities to form a reduced metal matrix consisting essentially of Fe-Al-Si and carburizing said titanium oxide to form as one phase titanium carbide with high combined carbon content close to theoretical value and less than 0.2% carbon as free carbon impurity in a single step, said titanium carbide being formed as an intimate mixture of titanium carbide grains surrounded by said metal matrix as another phase;

grinding said mixture of titanium carbide and metal matrix;

leaching said mixture with an aqueous solution of sulfuric acid and hydrofluoric acid; and recovering highly pure high combined carbon, titanium carbide grains.

2. The process according to claim 1 and wherein the titanium oxide containing material is Sorels slag, the metal matrix is a mixture of Fe-Al-Si with incidental amounts of other impurities associated with said Sorels slag, said aqueous solution used for leaching is a 1 to 2% aqueous solution of sulfuric acid and 0.3 to 1% aqueous solution of hydrofluoric acid.

3. The process according to claim 1 and wherein the leaching solution is 1 to 20% aqueous sulfuric acid and 0.1 to 3% hydrofluoric acid in a proper quantity.

4. The process according to claim 1 and wherein the temperature at which the starting material is reduced is from 2200° C. to the melting point and the period for heating is less than 20 minutes, after a substantially uniform temperature has been achieved throughout the starting material.

5. The process according to claim 1 wherein the volatile impurities are removed as an effluent from a reaction zone.

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